SYNTHESIS OF ZEOLITE A IN BATCH AND SEMI-BATCH REACTORS

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Abstract

Zeolite A is a crystalline aluminosilicate, represented by the formula $Na_{12}[(AlO_2)_{12}(SiO_2)_{12}]\ 27H_2O$. It has a wide range of applications as ion exchangers. One of these is in a detergent builder where it was suggested in 1970s to replace the phosphate builder for environmental reasons. This crystalline material is usually prepared by combining sources of silica, alumina and alkali to form an aluminosilicate gel.

Synthesis of zeolite A from sodium aluminate and sodium silicate solutions has been studied using batch and semibatch reactors. The experiments were performed to investigate the effect of the addition rate of sodium silicate solution on zeolite A crystallization. Samples were taken at one hour interval times. The solid samples were analyzed using x-ray diffraction and Scanning Electron Microscope.

The addition rate of sodium silicate influenced the nucleation and crystallization rates of zeolite A. Scanning Electron Micrograph of the solid samples indicated a change in the crystal habit and size due to change in the mode of operation from batch to semibatch reactors.

INTRODUCTION

Molecular sieve zeolites are a class of aluminosilicate compounds suitable for use in a variety of industrial process such as adsorption, separation and catalytic reaction due to their internal structure and surface characteristics. Zeolites are synthesized from alkaline aluminosilicate gel consisting of a heterogeneous phase in which amorphous solid and aqueous solution phases coexist. In 1987, 375,000 metric tons of zeolite A were produced worldwide only for the detergent industry. The product should be free of impurities and should have a small average particle size (approximately 4μm or less) and narrow particle size distribution.

Molecular sieve zeolites are synthesized primarily in batch crystallizer. There are only two known reports of continuous stirred tank syntheses (Culfaz et. al (1977), Culfaz et. al (1981)) and two known reports of tubular reactor syntheses (Rollman et. al (1980), Wolf et. al(1982)). Both of these reactor types give poorer performance (i.e. lower conversion, smaller crystal and ununiform size distribution) than the same sized batch reactor. Zeolites are often metastable and their formations depend not only on the

composition of the reaction mixture and the synthesis temperature, but also on the nature of the starting materials, method used to prepare the gel and the degree of agitation of the reactant.

The purpose of this present work is to report a recent study of zeolite crystallization in batch and semibatch crystallizer. In semibatch mode, crystallization is allowed to proceed during the time of the reactor is being filled and no effluent stream is withdrawn until the crystallization process is completed. The solid product from both reactors are analyzed using XRD, SEM, and Malvern Mastersizer.

EXPERIMENTAL

All experiments were carried out in a 2L stainless steel laboratory scale crystallizer at 100°C with reflux at ambient pressure. Stirring was constant at 700 rpm in each experiment using turbine type stirrer. Materials used in these experiments were Natrium Silicate, Natrium Aluminate and distilled water. 107.66 g of Natrium Aluminate (41 wt% Na_2O, 54 wt% Al_2O_3, 5 wt% H_2O)was dissolved in 1220ml of distilled water to make Natrium Aluminate solution. Natrium Silicate solution was prepared by adding 650ml water to 240 g Natrium Silicate (16 wt% Na_2O, 32 wt% SiO_2, 52 wt% H_2O).

For the batch process, Natrium Silicate solution was added to Natrium Aluminate solution in the crystallizer in a very short time. On the other hand, for semibatch process Natrium Silicate solution was added gradually into the crystallizer containing Natrium Aluminate. Sample were taken out from the reaction vessel at chosen time interval, filtered through a 0.2 mm membranes filter and separated into solid and liquid. The solid portion was washed with a large quantity of distilled water until the pH of wash is below 10, then dried overnight. in a oven at a temperature of 60°C. The solid sample was analyzed using XRD for qualitative and quantitative measurements. The crystal size distribution was determined by Malvern Mastersizer. The crystal morphology of the crystalline phase was examined using a Scanning Electron Microscope.

RESULTS AND DISCUSSION

The solid sample was analyzed for percent crystallinity, size, and morphology.

Percent Crystallinity

The percent crystallinity of zeolite A in the process was estimated using X-ray diffraction pattern of the sample. Percent crystallinity of zeolite A is defined from the ratio of the total peak area of a number of very intense peaks of the product sample to that of the reference sample. The crystallinity curves for both batch and semibatch processes were shown in Figure 1. Classical sigmoidal curves were obtained as usually observed for various zeolite crystallizing from non-seeded system(Hu et. al 1990, Tassopoulos et. al 1986 & 1987). Based on the plot, it can be concluded that the semibatch process requires shorter time for the zeolite to achieve 100% crystallinity. The addition rate of sodium silicate plays an important role in controlling the SiO2/Al2O3 ratio in the solution, and the ratio of SiO2/Al2O3 in the reaction mixture has some influence on the crystallization

process.. This finding also was in agreement with the result obtained by Hu et. al. (1990). They found that the rates of nucleation and crystallization decreased slightly and moderately respectively as the initial Al2O3 concentration was reduced for the same concentration of SiO2.

Based on the observation during experiment, the reaction mixture of lower addition rate of sodium silicate was less viscous as compared to higher addition rate of sodium silicate in semibatch and batch reactors.

Size Analysis

Size analyses of the solid sample were done using Malvern Mastersizer. The variation of particle median volume diameter (D(V,0.5)) with time in batch and semibatch crystallizers is shown in Figure 2. Median volume diameter is the diameter of particles having cumulative volume equal to 50% of the total volumes of particles. The result shown that the semibatch process with lower addition rates of sodium silicate produced larger crystal size than higher addition rates of sodium silicate or batch processes. Semibatch process produced larger crystal because the concentration of reactants in the reactor were lower, thus number of nuclei were small. Crystal with small number of nuclei will grow faster than crystal with large number of nuclei because of smaller surface area available.

Crystal Morphology

Scanning Electron Microscope was used to determine the morphology of the zeolite crystal. Micro graphs of zeolite A were shown in Figure 3. Crystals obtained in a batch system were cubic; on the other hand, crystals produced in a semibatch system were cubic with bevelled edges. The small different in shape is perhaps due to the influence of SiO_2/Al_2O_3 ratio in the reaction mixture. However, the precise nature of the morphological changes requires further clarification.

CONCLUSIONS

It has been shown that Zeolite A can be produced in high yields in a semibatch crystallizer. The controlled addition rate of sodium silicate over a certain period of time provides a means to control the precipitation kinetics of zeolite A in a semibatch crystallizer. Longer addition time reduces the induction period and increase the crystallization rate. The crystals produced in a semibatch mode were larger than those produced in a batch mode for the same reaction condition. The morphology of the crystals were affected by the mode of operation.

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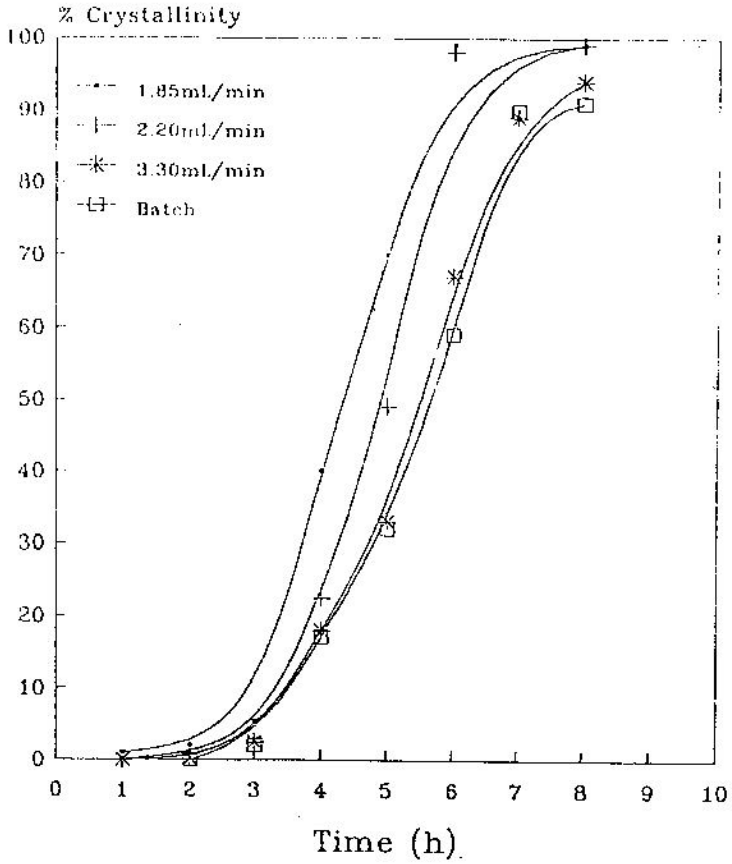

Figure 1: Changes of percent crystallinity of solid phases as a function of synthesis time

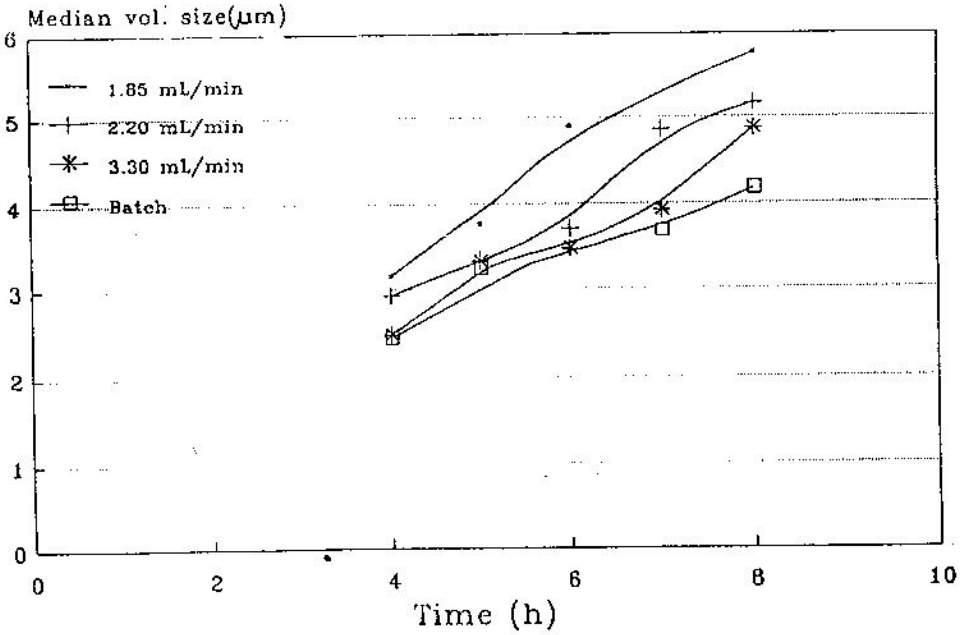

Figure 2: Variation of median volume diameter, D(V,0.5) of the particles with time for batch and semibatch crystallizers.

a)

b)

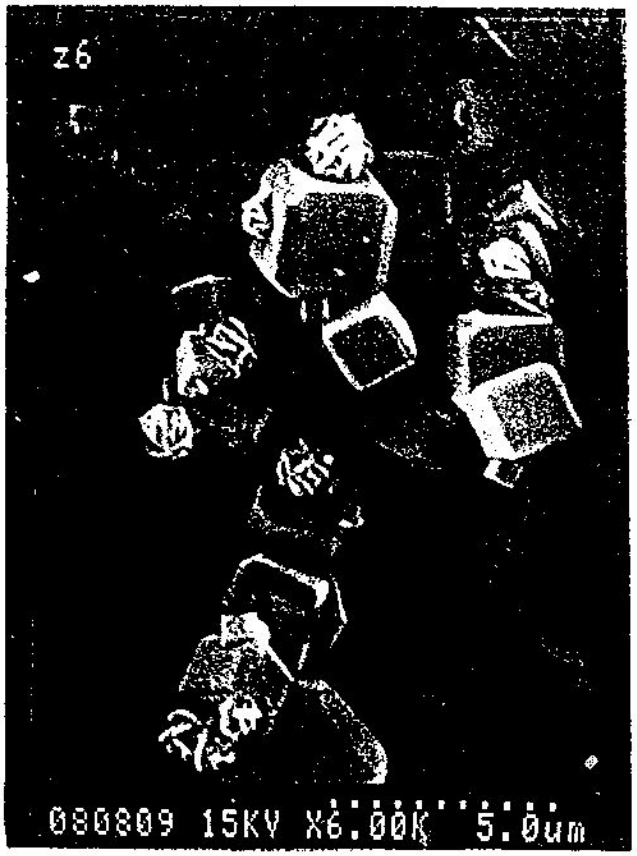

Figure 3: Scanning Electron Micrograph of zeolite A crystal for
a) Batch reactor b) Semibatch reactor